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RESEARCH PAPER

Carbon nanotube (CNT)–epoxy nanocomposites: a systematic investigation of CNT dispersion

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Abstract A systematic investigation of the dispersion of carbon nanotubes (CNTs), 1–6 nm in diameter and a few microns in length, in a bisphenol F-based epoxy resin has been presented. Several dispersing techniques including high-speed dissolver, ultrasonic bath/horn, 3-roll mill, etc. have been employed. Optical microscopy has been extensively used to systematically characterise the state of CNT dispersion in the epoxy resin during the entire processing cycle from mixing CNT with resin to adding and curing with hardener. Complimentary viscosity measurements were also performed at various stages of nanocomposite processing. A method to produce a good CNT dispersion in resin was established, but the state of CNT dispersion was found to be extremely sensitive to its physical and chemical environments. The cured nanocomposites were further tested for their thermo-mechanical properties by dynamic mechanical thermal analysis (DMTA), and for flexural and compressive mechanical properties. The measured properties of various nanocomposite plates were then discussed in view of the corresponding CNT dispersion.

Keywords Carbon nanotubes · Epoxy resin · Nanocomposites · Stability of dispersion · Dispersing agent · Optical microscopy · Mechanical properties · Flexural and compressive strengths

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Introduction

It is well known that carbon nanotubes offer enormous potential for a number of applications, thanks to their excellent mechanical (Treacy et al. 1996; Wong et al. 1997; Falvo et al. 1997, electrical (Hamada et al. 1992; Wildoer et al. 1998; Odom et al. 1998) and thermal properties (Kim et al. 2001). Out of many possible applications, mechanical reinforcement of polymers by incorporation of carbon nanotubes (CNTs) has received strong interest from the scientific community as well as the industry, especially since the beginning of the new millennium (Coleman et al. 2006; Thostenson and Chou 2006; Gojny et al. 2005; Chakraborty and Coleman 2008; Hubert et al. 2009). What makes CNTs very interesting for composites is that even with a relatively low level of loading (ca. 0.1–1 wt%), improvements in mechanical properties of polymers have been

reported (Hubert et al. 2009; Gojny et al. 2004). Yet there exist a number of challenges to be overcome in order for successful exploitation of the full potential of these tiny nanotubes of carbon. For example, obtaining a good dispersion of CNTs in the polymer matrix is very challenging and is known to be extremely important for successful mechanical reinforcement (Coleman et al. 2006; Thostenson and Chou 2006). Another challenge is to achieve a good interfacial bonding of the CNTs with the polymer matrix, generally absent given the chemical inertness of the CNT surfaces. The difficulty in dispersing CNTs arises from their inherently inert (hydrophobic) nature and tendency to agglomerate and entangle due to their size and shape (long hair-like). Reported literature addressing these challenges largely rely on chemical functionalization of CNTs (Suri et al. 2008; Coleman et al. 2007; Chakraborty et al. 2009; Martinez-Rubi et al. 2007) which requires expensive chemicals and therefore, is not commercially very attractive considering the cost involved. In addition, use of aggressive chemicals and strong dispersing methods such as prolonged ultrasonication can degrade the CNT intrinsic properties or even cut them shorter (Niyogi et al. 2002; Liu et al. 1998).

With epoxy resin matrices, the issue of dispersion is further complicated considering the differences from common polymers as most epoxy resins have two components—a resin and a hardener. Therefore, unlike dispersing methods reported for single component polymers (mostly thermoplastics), a method that facilitates a good CNT dispersion in an epoxy resin may not necessarily hold true after the hardener is added to the resin in which, suppose, the CNTs were well dispersed. In general, CNTs are dispersed in the resin first, and the hardener is added afterwards for curing. However, often the curing process requires long-time heating of the composites (Zhou et al. 2008). Thus, factors such as viscosity of the matrix, cure time, shear and temperature are likely to influence the state of an otherwise "good CNT dispersion" (as often described in the literature), which might have been obtained in the epoxy resin alone, once the hardener is added into the system.

Nevertheless, since epoxy resins require curing before being ready for any use, a good dispersion of CNTs is required not only in the resin alone but also in the cured final composite if the expected potential benefits of CNTs as reinforcing agent are to be achieved. An obstacle to systematic investigation of the CNT dispersion arises from the scientific and technological challenges in characterisation and interpretation of the observed results. As CNTs are made of carbon, a major constituent also of most polymer matrices, in which CNTs are dispersed, differentiating CNTs from their matrices is rather difficult even when direct characterisation methods such as electron microscopy is employed. Some researchers employed indirect methods such as viscosity or dynamic light scattering (DLS) to evaluate the state of CNT dispersion in epoxy resin. For example, Rahatekar et al. (2006) used rheological methods in which they correlated the measured shear-induced lowering of viscosity of the resin with the breaking of a well-connected network of CNTs or CNT aggregates. More recently, Kim et al. (2009b) employed DLS and differential scanning calorimetry (DSC) for characterisation of CNT dispersion. Here the authors linked the observed lowering of the total heat of reaction for curing caused by the addition of CNTs to the corresponding state of their dispersion.

Kovacs et al. (2007) extensively used scanning electron microscopy (SEM) to directly characterise CNT distribution in an epoxy matrix using the secondary electron imaging. While transmission and scanning electron microscopy techniques are perhaps the most direct methods to visualise the CNT distribution in nanoscale, they lack in that they can be used for the characterisation of the *cured* epoxy composites only. Electron microscopies suffer from difficulty in sample preparation which prevents their use in real-time investigation during composite processing. A further limitation is that images acquired with these techniques represent relatively small area and one has to take specimens from a number of locations of a sample and obtain numerous images from numerous locations of each specimen to draw any conclusion on the quality of the CNT dispersion over the entire sample. Any quick conclusion drawn from these methods (say, for example, from only a few images) can be misleading, and hence sufficient care must be taken when using these methods. This means that using these techniques and analysing the data could be quite tedious and time-consuming.

Optical microscopy, on the other hand, with its relative ease of use, can directly provide information on the state of dispersion in real time, both in liquid

resin and in cured solid composite. Even though some researchers (Sumfleth et al. 2008; Rosca and Hoa 2009) have used this method to characterise CNT dispersion in epoxy resins, its potential has not been fully utilised for real-time monitoring of the dispersion during curing. The need for recording systematic images as a function of time and temperature before and after adding the hardener has been somewhat overlooked. With its simplicity combined with relatively large sampling area and fast measurement, optical microscopy has great potential in following the state of a CNT dispersion in real time during curing of thermosetting polymers like epoxy resins. The only work in which this issue has been *partially* addressed using optical microscopy have been published very recently by Ma et al. (2010) which came to our notice during the write up of this manuscript. Here the authors have monitored the change in the state of CNT dispersion in an epoxy resin after adding hardener as a function of time. However, the epoxy resin, hardener and CNTs used in that study are different from those used in this work, and the processing methods are also entirely different from that reported in this article. They used solvent-based ultrasonication method to disperse CNTs in the epoxy resin which may not produce very good CNT dispersion (as observed in this paper) in epoxies.

In this work, we present a systematic investigation of the dispersion of CNTs in an epoxy matrix using primarily optical microscopy. Several approaches have been reported in the literature to facilitate good dispersion of CNTs in epoxy matrix. Among them are mechanical mixing (by methods such as ultrasonication, ball milling, calendering, etc.), chemical functionalization, polymer wrapping, surfactant wrapping, etc. (Coleman et al. 2006). We first explored the use of different dispersing tools such as ultrasonic horn/bath, high shear mixer, 3-roll mill or a combination of one or more of the above to establish a method that gives the best CNT dispersion. Prolonged use of these methods is known to cause damage to the CNT intrinsic properties and should be avoided. To obtain improved CNT dispersion without significantly damaging the CNT intrinsic properties, we, therefore, chose to use commercial dispersing agents (DAs) which are known to help CNTs separate from bundles and suspend in the epoxy matrix. To the best of our knowledge, this is one of the very few reports in which the state of CNT dispersion in an epoxy resin has been systematically monitored using optical microscopy as the primary technique during the entire processing cycle from mixing CNTs with resin to adding and curing with hardener. To complement the optical microscopy data, we also recorded viscosity data at various stages of CNT dispersion. The cured nanocomposites were further tested for their thermo-mechanical properties using methods such as DMTA, flexural, and compressive mechanical tests. The measured thermal and mechanical properties were then associated with the observed dispersion of CNTs in the corresponding composite samples. Overall, this article is predominantly focused on the systematic investigation of the physico-chemical processes associated with the dispersion of CNTs in the epoxy resin alone as well as during the process of curing of the composites after the addition of the hardener. It is further noted that the motivation of this work is to improve the mechanical properties of thermosetting resin matrices using CNTs in very small weight fraction to be used in fibre-reinforced composites with the ultimate aim of improving their matrix-dominated properties such as delamination and interlaminar shear strength.

Experimental

Materials

CNTs (XD grade) used in this work (Unidym, Inc., USA) consisted of a mixture of single wall, double wall, and triple wall CNTs with single-wall CNTs being the dominant fraction (Kim et al. 2009a; Tao et al. 2006). The carbon content is claimed to be more than 95 wt% in the sample (Kim et al. 2009a) with diameters and lengths in the range of 1–6 nm and 1–5 microns (Thuau et al. 2009), respectively (see Fig. 1). This type of CNTs was chosen for their proven characteristics and influence on the mechanical properties of epoxy resins (Zhou et al. 2008; Bekyarova et al. 2007). The epoxy resin Epikote 862 and hardener Epikure 3402 (Hexion, Germany) were used as the matrix material. Epikote 862 resin is a bisphenol F-based epoxy, and Epikure 3402 is diethyltoluenediamine as per the supplier's specification. The resin and the hardener were chosen for their relatively low viscosity and long potlife (several hours even at 80 °C) allowing sufficient time for processing and

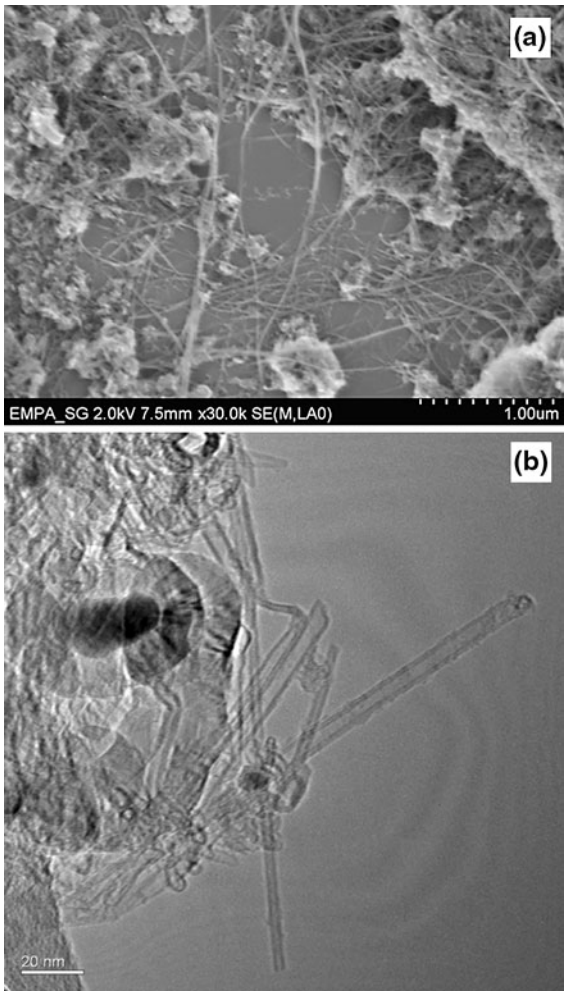

Fig. 1 High-resolution SEM (**a**) and TEM (**b**) images of as-received XD grade CNT raw material. Hair-like features are CNTs or CNT bundles, while other bright features correspond to amorphous carbon

characterisation of the samples and, therefore, attracted many researchers (Zhou et al. 2008; Rosca and Hoa 2009; Bekyarova et al. 2007) in the recent years to investigate the influence of CNTs on their mechanical properties. Dispersing agent BYK 9077 (BYK Chemie, Germany), which is a high molecular weight copolymer with pigment affinic groups as per the supplier, was chosen for its known positive influence in dispersing CNTs (Xia and Song 2005).

Sample preparation

At first, appropriate amount of DA (typically 1.5 g) was weighted in a metal can to which approximately 120 g of epoxy resin Epikote 862 was added. Generally, DAs are first dissolved in a volatile organic solvent and then CNTs are dispersed in the liquid media as a starting step before adding the epoxy resin. In this work, however, the DA was directly added to the resin to avoid possible risk of residual solvent which can degrade the mechanical properties of the final composites. Required amounts (typically 0.3 g) of CNTs were then weighted and added to the metal can, and then hand-mixed for a few minutes in order to wet all CNTs with the resin. In the next step, this mixture was further homogenised using a variety of dispersing tools including high speed dissolver (Dispermat CV2 by VMA-Getzmann, Germany), ultrasonic horn (Bandelin sonoplus 2200, Germany), and ultrasonic bath (Bandelin sonorex, Germany). One or more of these techniques were employed to improve the dispersion of CNTs in the resin. However, all samples discussed here except in Fig. 2a, c were prepared using the high-speed dissolver operated for 15 min at 8,000 rpm for reasons described later. Then, further dispersion was achieved by passing the pre-mixed resin through a 3-roll mill (Bühler SDY200, Switzerland) for 10 cycles.

In the next step, irrespective of the choice of the mixing methods used, the obtained resin mix was further mixed with the appropriate amount of hardener (26.4 parts to 100 parts of resin in weight). Here, the hardener was first hand mixed for a few minutes after which a planetary mixer (Planimax by Molteni, Italy) running at a speed of 150 rpm under vacuum (below 100 mbar) was used for 15–45 min either at room temperature (RT) or at 80 °C. Heating was necessary in order to lower the viscosity and thereby to improve the efficiency of vacuum degassing to minimise entrapped air bubbles in the cured composites. In particular, the choice of 80 °C as the mixing temperature was made, as this was a temperature that allowed sufficient time available for mixing and processing of the composite before it gelled. Higher temperatures would have reduced the viscosity further but would allow much less time for processing. Next, the composite mixtures were cast in steel mould to make composite plates. The curing of the composite plates was done by heating the mould at 120 °C for 4 h followed by a further 4 h heating at 170 °C in an oven in air following the protocol reported for the same system by Zhou et al. (2008).

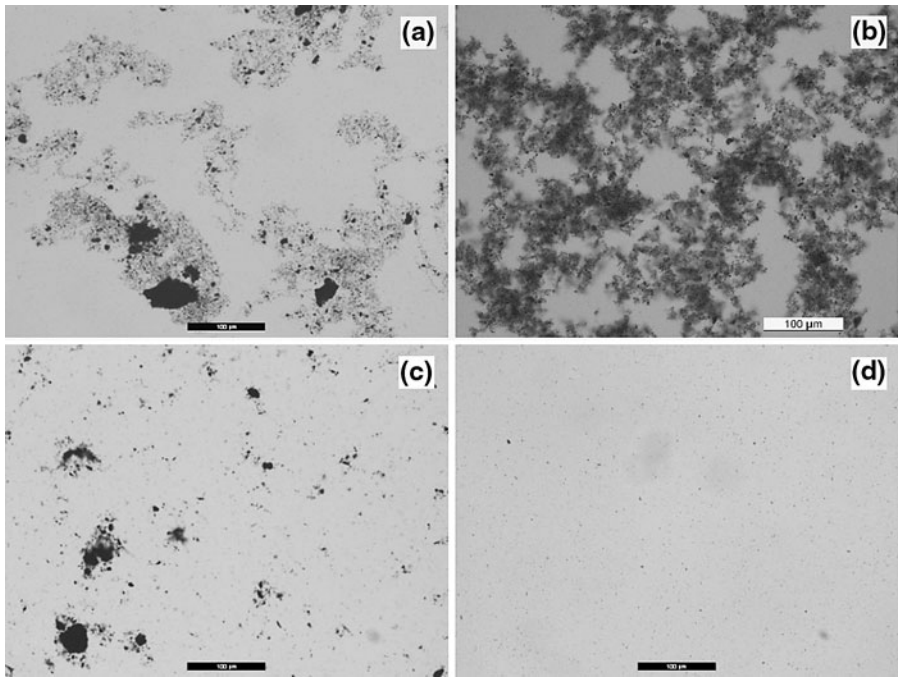

Fig. 2 Optical images recorded on CNT-dispersion in resin alone obtained using **a** high-speed dissolver, **b** ultrasonic horn, **c** high-speed dissolver + ultrasonic bath, **d** high-speed dissolver + 3-roll mill (10 passes). *Scale bar* is 100 µm

The cured composite plates were machined using a diamond saw to prepare specimens of required sizes for various tests.

For systematic comparison of the mechanical properties, samples were prepared with various combinations of components as listed in Table 1. The idea behind the selection was to compare and separate effects of CNTs and DA on composites mechanical properties. In addition, as the investigation of dispersion mainly involved samples prepared with 0.2 wt% CNTs, which, if considered, is rather low for imparting a significant influence on mechanical properties, a composite plate was also prepared with 1 wt% CNTs.

Table 1 Material composition for different nanocomposite samples

Sample	CNT wt%	DA wt%
A	0	0
B	0	1
C	0.2	1
D	0.2	8
E	1.0	1

Characterisation

Rheology

Viscosity data were recorded by a ARES rheometer (Rheometric Scientific) using parallel plate geometry with a fixed gap of 0.5 mm. Data were recorded in dynamic strain sweep (oscillatory) mode at a fixed frequency of 15 Hz at room temperature (25 °C) between strains of 1 and 2,000%.

Optical microscopy

Optical images were recorded in transmission mode using a microscope (Axioplan by Zeiss, Germany) equipped with a camera (Leica microsystems, Germany) with a 20× objective lens offering lateral resolutions better than 5 microns. Samples were prepared for optical imaging by taking a small droplet of the composites, at different stages of sample preparation, on a glass slide and then pressed with another glass slide on top with a fixed load for a fixed time. To avoid any variation due to different delay time from sample preparation to imaging, where

possible, we imaged the samples immediately after preparation of the glass slides. Where this was not possible, a suitable time delay was chosen and kept constant for all samples. Typically, samples were taken immediately after the CNTs were just dispersed in resin alone, after mixing the hardener, and after the composites were cured. Additional samples were also prepared at other intermediate stages but not all are presented here.

Electron microscopy

Fracture surfaces of composite specimens obtained by 3 point bending test were coated with a thin layer (4 nm) of platinum before imaging in a JEOL JSM 6300F SEM system. SEM images of CNT raw material were acquired with a Hitachi S-4200 microscope and the transmission electron microscopy (TEM) images with a Phillips CM 30 microscope.

DMTA

Specimens were characterised using an Eplexor 500 N (Gabo Qualimeter, Germany) dynamic mechanical and thermal spectrometer operating in tension. Specimens were cut in dimensions of $60 \times 10 \times 4$ mm. All data were recorded using a load cell of 500 N at a heating rate of 2 °C/min with a step of 2 °C and at 10 Hz frequency between 20 °C and 220 °C.

Flexural test

Flexural tests were performed with universal testing machine (Zwick Z1474) controlled by the TestXpert software following the standards of ASTM D790. Specimens of dimension $80 \times 10 \times 4$ mm with 64 mm span were subjected to load at the centre from a 1-kN load cell. Displacement-controlled tests were performed at a speed of 5 mm/min.

Compression test

Plane strain compressive tests were performed with a universal testing machine (Zwick Z010) with a 10-kN load cell. Displacement-controlled experiments were performed at a rate of 0.5 mm/min according to a method developed by Williams and Ford (1964).

Results and discussion

Before presenting optical images of CNT-epoxy composites to assess the quality of CNT distribution, it is noted that by good dispersion, we mean a state in which not many dark spots/features are visible in the optical image. The aggregates of CNTs are likely to have larger size (microns) than individual CNTs (nanometres) and hence light will be scattered more readily from the aggregates which will make them easily visible (as dark spots) in the optical microscope, and hence dark spots in the images should indicate aggregates of CNTs. An image without dark spots does not necessarily indicate absence of aggregates but at least that the aggregates are smaller in size than the ones in which many dark spots are visible.

For proper comparison, certain parameters were fixed for all samples. In all data shown here for comparison of CNT dispersion, a fixed concentration of CNTs (0.2 wt%) was maintained. The CNT concentration of 0.2 wt% was chosen such that the improvement in mechanical properties occurs at a very low effective loading level, vital for commercial applications. It was observed that with 0.2 wt% CNT loading, Zhou et al. (2008) improved the flexural strength by 22% for the same epoxy resin as that in the current work. Higher loading would also mean that CNTs are too close to each other causing the optical images to be almost black in which it would be impossible to differentiate the dispersion as a function of various influencing factors. Loading lower than 0.2 wt% was not considered an option because too low loading of CNTs might not impart measurable reinforcing effect on the matrix, and if so, the results of the current investigation would be rather difficult to interpret. The amount of surfactant (where used) was kept constant at 1 wt% (5 times CNT mass) of the total composite, except for the sample D for which 8 wt% (40 times CNT mass). For sample E, the ratio of DA to CNT was kept at only 1:1 (1 wt%) to avoid excess amount of DA.

Figure 1a presents an SEM image of the CNT raw material, in which randomly oriented long hair-like CNTs are observed. It is evident that the diameter of the CNTs varies between ca. 5 and 30 nm, indicating presence of some thicker CNTs or bundles of CNTs. Presence of some amorphous material is also observed along with CNTs. Figure 1b is a

representative high-resolution TEM image of the same CNT raw material showing a single CNT protruding out of a large aggregate.

Figure 2 presents a series of images recorded on CNT dispersions in epoxy resin immediately after their preparation using various dispersing techniques. Figure 2a and b corresponds to the samples prepared using a high-speed dissolver (Dispermat) rotating at 8,000 rpm for 15 min and an ultrasonic horn operating at 40% amplitude for 60 min at pulses (ON) of 70%, respectively. Image shown in Figure 2c was obtained from a sample prepared following the method shown in Fig. 2a followed by sonication for a further 1 h in an ultrasonic bath. Figure 2d corresponds to a sample prepared following the method shown in Fig. 2a followed by ten passes in a 3-roll mill. All images presented in Figs. 2, 3 and 4 were acquired with the same magnification. It is obvious that the best dispersion of CNTs is achieved when the high-speed dissolver followed by ten passes in the 3-roll mill was used because the image shown in Fig. 2d does not show presence of many dark spots.

It is worth noting that all dispersion methods presented in Fig. 2 involved the addition of the DA (5 times CNT mass) because the dispersions achieved without it were very poor (not shown here). Nevertheless, in Fig. 3, two images are shown in which the role of DA on CNT dispersion has been demonstrated only for the special case of the samples prepared following the method in Fig. 2d. Here the image in Fig. 3a has many dark features as it was produced without DA, but the image in Fig. 3b is almost transparent with no dark features, which was produced with 8 wt% DA. Thus, it can be said that even with the use of 3-roll mill, aggregates of CNTs are present when no DA is used. It is also interesting to note that the images shown in Figs. 2d and 3b are both recorded on samples produced by the same processing conditions except that the DA amount increased from 1 to 8 wt% from the former to the later. A close look reveals virtually no difference in the optical images of the two samples suggesting no need of using 8 wt% DA. Therefore, in order to minimise any possible degradation of the mechanical properties of composites coming from the DA, all samples were processed with 1 wt% DA except for the sample D (8 wt%) which was prepared to explore the influence of DA in mechanical properties of the nanocomposite.

As we established a processing methodology to obtain a good CNT dispersion in resin (method in Fig. 2d), all samples prepared and all data shown hereafter correspond to this dispersing method. However, one may ask if this state of good dispersion will remain unperturbed by external conditions such as time and temperature. From a practical point of view, it may be necessary that such dispersion is stored or transported for sufficiently long time before its use. To get information on the state of dispersion in resin as a function of time, we recorded images at various intervals from their time of preparation. Figure 4 presents optical images recorded on CNT dispersions as a function of time delay from the time of production. After the CNT-resin mixture is stored for 16 h at room temperature, the image in Fig. 4b looks a little bit darker indicating slight coagulation of CNTs, but overall the integrity of the dispersion remained rather unaltered. Figure 5 shows a comparison of the viscosity (η^*) against per cent strain (γ) of the CNT-resin mix under the influence of various

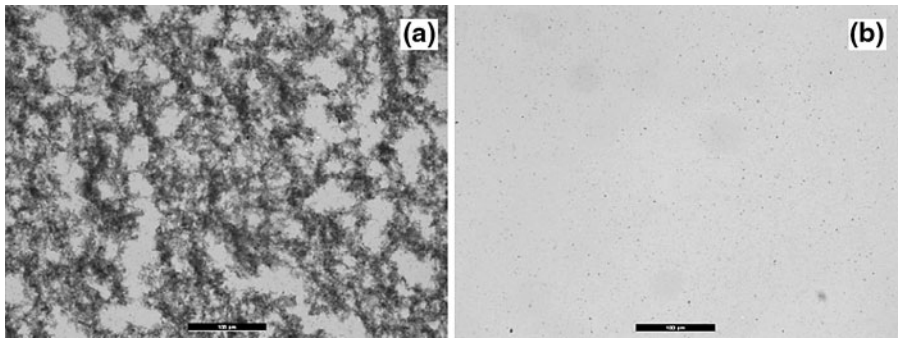

Fig. 3 Optical images recorded on CNT-dispersion in resin obtained using high-speed dissolver + 3-roll mill (10 passes), in the **a** absence, and **b** presence of DA (40 × CNT mass). *Scale bar* is 100 μm

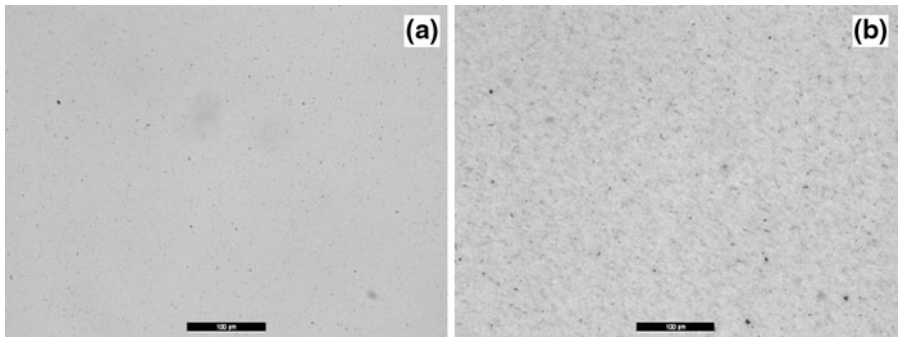

Fig. 4 Optical images recorded on CNT-dispersion in resin alone obtained using high-speed dissolver + 3-roll mill (10 passes): **a** immediately after preparation and **b** after 16 h at RT. *Scale bar* is 100 μm

external factors such as storage time and heat. The curves in Fig. 4a–c respectively represent the viscosities of the resin without CNTs, CNT-resin mix immediately after preparation, and after storage at room temperature for 16 h. It is clear that the viscosity sharply increases with the addition of CNTs in the resin, but remains almost unaltered when the resin containing well-dispersed CNTs (Fig. 4b) is stored at room temperature for 16 h (Fig. 4c).

It is worth noting that all images in Figs. 2, 3 and 4 were recorded on samples kept at room temperature. One may ask what happens if the temperature is raised above room temperature, especially since many epoxy resins require heating above room temperature for curing, a process by which the viscosity of the resin can drop significantly depending on the temperature to which it is heated. Such a large variation in viscosity could be detrimental to the stability of CNT dispersion in the matrix. In order to explore the influence of heat on the state of CNT dispersion on resin alone, we recorded optical images of CNT dispersion as a function of temperature as depicted in Fig. 6. Here we observe that the dispersion of CNT is almost stable when the temperature is raised (to 80 °C) for a relatively short period of time (1 h) (Fig. 6b); the longer one heats it (4 h) the more disturbed it gets as indicated by the blackening of the image in Fig. 6c. Further support to the optical microscopy data was obtained from the corresponding viscosity measurements as shown in Fig. 5. The viscosity of the CNT/resin mix increased after it was heated at 80 °C for 1 h (curve d) which increased further when heated for 4 h (curve e). This is in agreement with the results of viscosity measurements by Godara et al. (2009) in which the authors reported

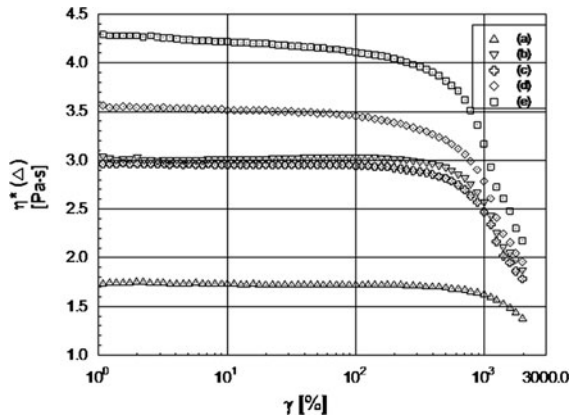

Fig. 5 Comparison of viscosities of CNT-resin mix under the influence of various factors: (*a*) pure resin, (*b*) as prepared CNT-resin mix, (*c*) after mixture in 'b' was stored at RT for 16 h, (*d*) after mixture in 'b' was stored at 80 °C for 1 h, (*e*) after mixture in 'b' was stored at 80 °C for 4 h

an erratic viscosity profile (increase) and suggested that a re-agglomeration of unmodified MWNTs (due to poor affinity with epoxy) when heated above 70 °C (low viscosity) was responsible for the observed. The authors further explained that the apparent erratic increase in the viscosity resulted from the friction between the lumps of CNT aggregates produced by the two parallel rotating plates of the rheological instrument. The authors, however, were unable to confirm this hypothesis by any direct measurement, for example, using optical microscopy because the CNT concentration used in their work was too high (0.5 wt%) to be optically differentiated. In the current work, thanks to the optical images shown in Fig. 6, we confirm the agglomerate formation at elevated temperature as the primary reason for the increased viscosity. Nevertheless, the formation of aggregates

of CNTs from a well-dispersed system, in the absence of DA, can be explained in terms of the reduced viscosity and increased particle mobility which allow the particles to easily come close to each other and then form agglomerates due to van der Waals force. Their (CNTs') typical high incompatibility with polar matrices such as epoxy resins also assists it (Godara et al. 2009). In the present work, where a DA has been used purposefully to facilitate better CNT dispersion, re-agglomeration of CNTs is rather surprising as one would expect the polar groups of the DA will prevent it by chemical interaction. To understand why re-agglomeration occurs, we note that the relative concentration of DA compared to CNT may be less than what is required. CNTs are unlikely to be all separated and suspended as individuals by the DA and the dispersing methods employed; some can remain as small bundles with no DA attached to them and, therefore, can act as nucleating source when mobility of the matrix is increased. Given the unknown molecular weight of CNTs, and of the commercial DA, it is not possible to estimate the suitable ratio in which CNTs and DA are to be mixed. The choice of 1:5 ratio for CNT to DA in this work was made only because it produced a good dispersion at RT according to the optical images. One also has to keep in mind that the content of the DA should be kept as low as possible because its presence could degrade the mechanical properties of composites. All these factors together pose a serious challenge in finding the correct ratio of DA to CNT.

Having characterised the dispersion of CNTs in the epoxy resin alone, it was time to know the behaviour after adding the hardener without which the composites cannot be cured. Figure 7a shows an image recorded on a sample taken immediately after mixing-degassing with hardener for 15 min at RT, and Fig. 7b represents the same after it was stored at RT for a further 16 h. These images clearly suggest formation of CNT agglomerates as the dark patches of worm-like features become visible in the image even after first 15 min of mixing, as shown in Fig. 7a and they grow further in size after 16 h of storage at RT (Fig. 7b). This observation also suggests that the hardener addition alone is enough to destabilise the dispersion even when no time delay or heat is involved. As we raised the mixing temperature to 80 °C, the image recorded immediately after 15 min of mixing-degassing with the hardener (Fig. 7c) did not show much of a difference with that shown in Fig. 7a, indicating a rather insignificant role of temperature in the process. However, when this is further heated at 120 °C, the temperature at which the current resin system is supposed to be cured for best performance, the small aggregates of worms eventually join together to form long-strand-like features within minutes (5 min), Fig. 7d. Further heating at the same temperature causes very little change in the state of dispersion as the images recorded on samples heated for 1 h (partially cured) and 4 h (fully cured) are (not shown here) almost identical to the one shown in Fig. 7d.

Figure 7 shows that even though we started off with an epoxy resin mixture in which CNTs had been rather well dispersed; it was lost once the hardener had been mixed, be it at room temperature or at a higher temperature. As we know that the hardener is a must for curing of epoxy resins and often curing requires temperatures above RT, this observation can be considered very significant for the development of CNT-based epoxy nanocomposites and their

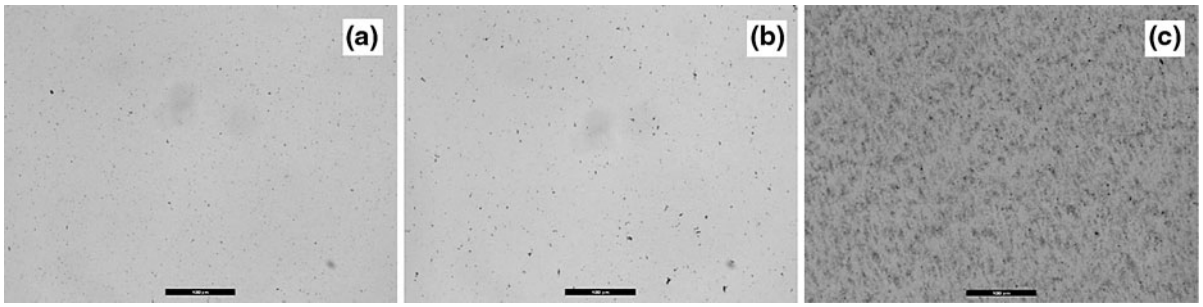

Fig. 6 Optical images recorded on CNT-dispersion in resin alone obtained using high-speed dissolver + 3-roll mill (10 passes): **a** immediately after preparation, **b** after heating at 80 °C for 1 h, **c** after heating at 80 °C for 4 h. *Scale bar* is 100 μm

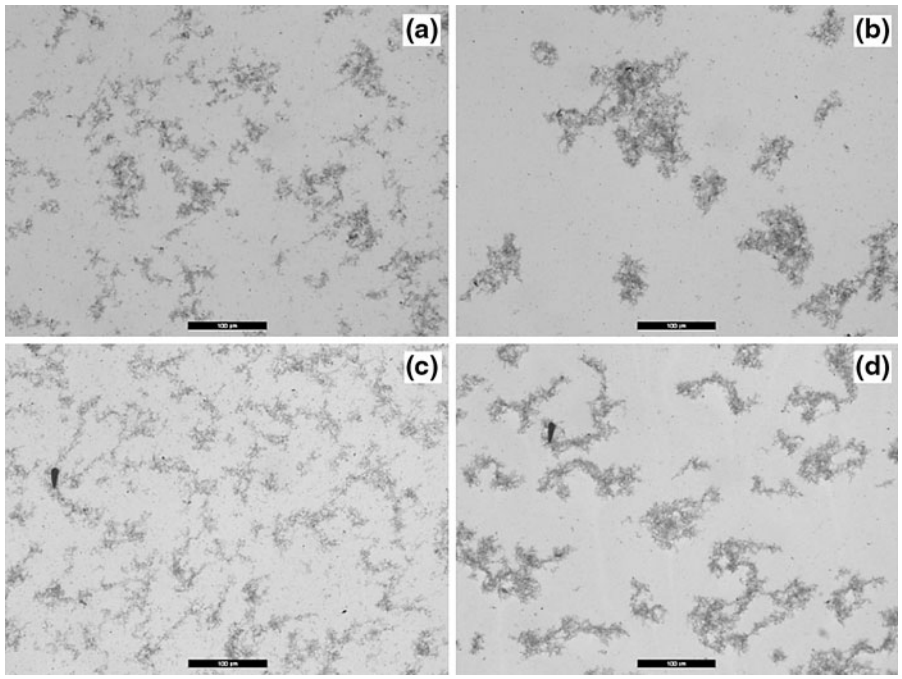

Fig. 7 Optical images recorded on CNT-dispersion: after the hardener was mixed for 15 min at RT (**a**); after sample (**a**) was stored for 16 h at RT (**b**); immediately after the hardener was mixed at 80 °C for 15 min (**c**); and after sample (**c**) was further heated at 120 °C for 5 min (**d**). Pre-dispersion of CNTs in resin was obtained using a high-speed dissolver + a 3-roll mill (10 passes). Scale bar is 100 μm

products. Unfortunately, even though several published articles have been directed to achieve a good dispersion of CNTs in matrices, the issue of the stability has remained rather unaddressed in the literature as little or no importance has been given to the significance of the re-agglomeration of CNTs in resin after mixing the hardener. To understand why re-agglomeration occurs upon hardener addition, it is noted that the addition of hardener lowers the viscosity (hardeners generally has lower viscosity than resin) even when no external heat is supplied. Mixing with the hardener introduces shear into the system which further alters the equilibrium of the system. As discussed before, in this complex system in which several physical and chemical processes occur simultaneously, any CNTs unwrapped by DA will form agglomerates due to increased mobility and van der Waals force of attraction even at RT. As the temperature is increased, the mobility increases and more agglomerates come in contact to each other to form large agglomerates or strands as seen in Fig. 7d. When the nanocomposite is stored at RT (well below its curing temperature) after mixing the hardener, for a long period of time as shown in Fig. 7b, even though the mobility of particles is increased due to lowering of viscosity by hardener addition, but the increase is relatively small compared to that at high temperature. Therefore, the formation of agglomerates occurs at slow rate as seen in Fig. 7b which was recorded after 16 h.

The morphology of the cured nanocomposites was further characterised by SEM. Figure 8 compares the representative images recorded on fractured surfaces of the cured composites manufactured with different amounts of CNT and DA. Images Fig. 8a to c all have same CNT content of 0.2 wt%, but the content of DA varied from 0 to 1 to 8 wt%, respectively. The image in Fig. 8d has 1 wt% CNT and equal amount of DA. The relatively bright spots protruding from the dark background may be assigned to the CNTs (Kovacs et al. 2007). It is not easy to "see" CNTs in the images, and drawing any conclusion on the quality of CNT dispersion from these images is, therefore, not possible. This further justifies our choice of optical microscopy as the method for systematic investigation of CNT dispersion.

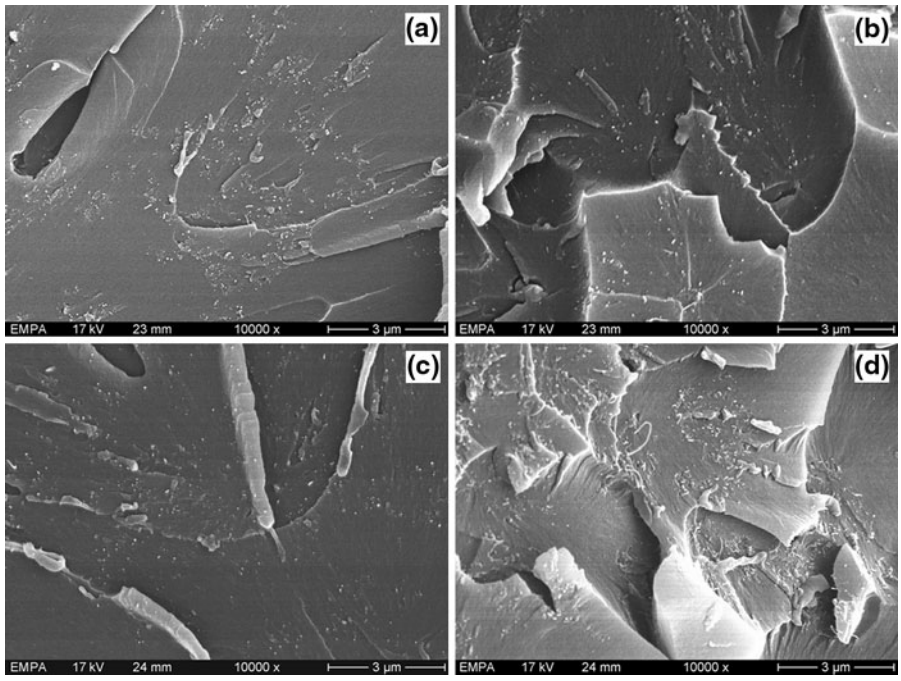

Fig. 8 SEM images of fractured surfaces of cured composites containing: **a** 0.2 wt% CNT, no DA; **b** 0.2 wt% CNT, 1 wt% DA; **c** 1wt.% CNT, 1 wt% DA; and **d** 0.2 wt%, 8 wt% DA. *Scale bar* is 3 µm

Let us now focus on the properties of the cured composites. At first, we show, in Fig. 9, the results of dynamic mechanical analysis of nanocomposite plates prepared following the same processing conditions as described in Fig. 2d with small variations in CNT or DA content from sample to sample (sample A to E, see Table 1). The elastic part of the complex modulus (storage modulus, E′) is plotted in Fig. 9a, and the loss factor (tan delta), measured by the ratio of storage to loss modulus, is plotted in Fig. 9b. The position of the peak in the plot of tan delta is often used as the glass transition temperature (T_g) and is a characteristic property of polymers. It is evident in Fig. 9 that almost no difference in magnitude of the moduli is observed from sample to sample except for sample D which shows a significant lowering of the temperature at which the rapid fall of E′ occurs Fig. 9a and the position of the T_g is shifted by at least 20 °C in Fig. 9b. The major difference in sample preparation for sample D lies in that it contains 8% DA (40 times CNT mass). Therefore, it can be inferred that the presence of DA in large amount (8 wt%) is responsible for this lowering of T_g even though its presence of 1wt% did not cause any noticeable changes in T_g. This result

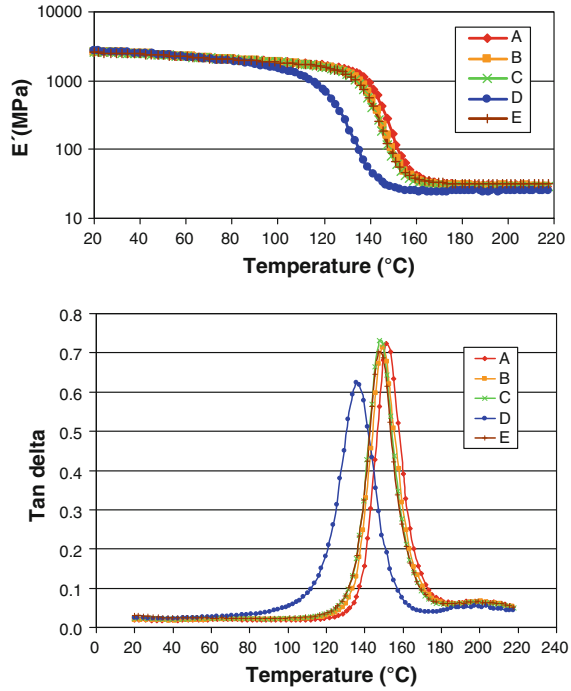

Fig. 9 Plot of storage moduli (**a**) and tan delta (**b**) versus temperature of various nanocomposite samples. See Table 1 for composition of samples from *A* to *E*

also suggests that the use of DA must be restricted to the minimum level needed for aid in dispersion. The value of T_g is altered for polymer matrices when the mobility of the molecules is influenced by the presence of foreign materials. It is evident that 8% DA causes a softening effect on the polymer possibly by allowing space for the resin molecules to move with ease, even though the storage modulus (E′) does not indicate any change at RT. On the other hand, presence of CNTs is generally expected to cause an increase in the T_g if CNTs are thought of as sites of obstructions to the mobility of resin molecules. However, it is worth noting that in a highly cross-linked epoxy resin system, it is not as much likely as in thermoplastic polymers to see a strong influence of CNTs in the T_g (Ci and Bai 2006). Lack of well-dispersed CNTs in the matrix further contributes to reduce such scope as the aggregates of CNTs are possibly separated by isolated regions of resin where no CNTs are present.

Figure 10 shows the flexural and compressive strengths of the different composite samples. While the strengths of the nanocomposites are expected to improve with CNT loading, this is not evident from the data. Even at the highest CNT loading (1 wt%) of this study, the flexural strength only increases from 114 MPa to 117 MPa, whereas the compressive strength drops slightly. Interestingly, for sample D, with 8 wt% DA content, a rather significant decrease is observed in the compressive strength (128 MPa) compared to that of the neat composite (135 MPa), indicating a contrasting role of the DA on the mechanical properties of the composites under flexure and compression. Figure 11 shows the corresponding flexural and compressive moduli of different samples indicating little or no influence of CNTs. All these results seem very surprising at first, considering there are so many articles in the published literature showing moderate to significant increases of mechanical properties of composites filled with CNTs. Of particular interest is the work of Zhou et al. (2008) which showed up to 22% improvements in flexural strength of the same resin for 0.2 wt% CNT loading and the corresponding flexural modulus (as deduced from the article) increased from 2.45 to 2.6 GPa for the same CNT loading. A careful observation of their results, however, reveals that the strength value of the neat composites (ca. 94 MPa) was far below that reported in the present work (ca. 114 MPa). In fact, the reported value of flexural strength by Zhou et al. (2008) for 0.2 wt% CNT loading reached ca. 116 MPa which is almost equal to the that of the neat composite in our work. The exact reason for such discrepancy is difficult to explain as the history of the samples in the work of Zhou et al. is not known to us; however, in this context, it becomes more interesting when one refers to the work of Ci and Bai (2006) in which the authors observed (experimentally) that the mechanical properties of a resin system with higher stiffness (elastic modulus value of 2.5 GPa or above) remained almost unaffected when loaded with CNTs. The authors associated this primarily with the lack of good interaction of CNTs with the resin.

Combined with non-existence of a stable and homogeneous dispersion in the cured composites as observed in this manuscript, the measured

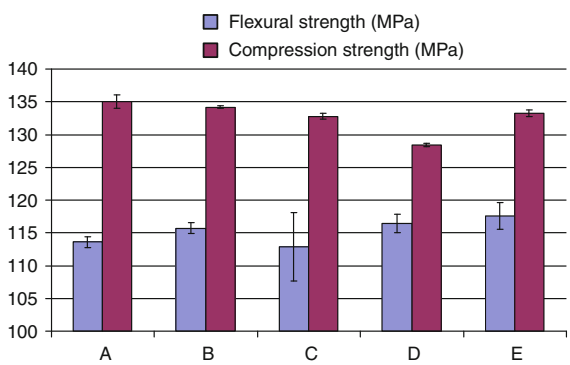

Fig. 10 Flexural and compressive strengths of different nanocomposite samples. See Table 1 for composition of samples from *A* to *E*

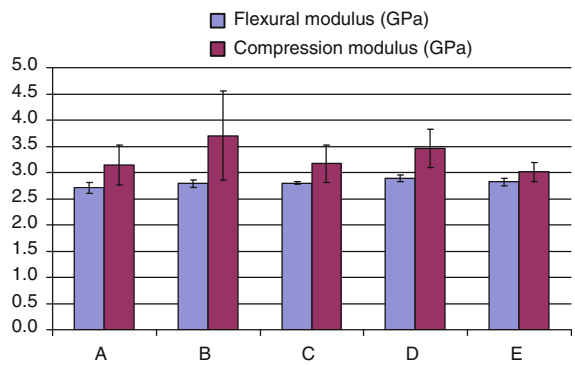

Fig. 11 Flexural and compressive moduli of different nanocomposite samples. See Table 1 for composition of samples from *A* to *E*

mechanical properties of the composites are perhaps not surprising. Recently, Bekyarova et al. (2007) proposed chemical functionalization of CNTs in order for CNTs to be stabilised in the epoxy matrix, even though the stability of dispersion was not proved by systematic investigation. The idea here was that through the functional group on their surfaces, CNTs can interact chemically with the epoxy resin, and thus, further addition of hardener should not significantly influence the dispersion as CNTs are chemically bound within the resin molecules. More recently, Ma et al. (2010) also employed a chemical functionalization approach to stabilise the dispersion of CNTs in epoxy resins. Another factor to consider is the very reason why CNTs are considered for mechanical reinforcement, i.e., their exceptionally good intrinsic mechanical properties. With strong dispersing methods, such as the one reported here, some mechanical damage to the CNTs in the form of defect formation as well as shortening of CNTs cannot be completely ruled out (Kovacs et al. 2009). All these factors can contribute to various degrees resulting in lack of expected improvement in the mechanical properties of the composites. Nevertheless, chemical functionalization offers a possibility to improve and stabilise the CNT dispersion as well as interfacial interaction with the matrix and is, therefore, currently under investigation to overcome the problems reported in this article.

Conclusion

In conclusion, a systematic investigation of the dispersion of CNTs in an epoxy resin system along with the mechanical properties of the cured nanocomposites has been presented. Optical microscopy has been utilised extensively for real-time monitoring of CNT dispersion in composites starting from the state of pre-mixing in resin alone to adding the hardener and to curing of the composites. We established a method using a 3-roll mill and a commercial DA which gave a good dispersion of CNTs in resin alone. However, such a good dispersion was found to be completely lost with the addition of the hardener as re-agglomeration occurred. Aggregates of CNTs separated from one another were clearly visible in composite samples after adding hardener and after cure. It was also observed that a good CNT dispersion in resin alone is also not very stable over a long period of time or at an elevated temperature, thus suggesting the need for paying extra attention when using masterbatches of CNT pre-dispersed resins. It is suggested that the chemistry of the hardener, together with physical factors such as high temperature, and associated lowering of viscosity are responsible for the destabilisation of the pre-existing good CNT dispersion in resin. The glass transition temperature was not influenced by the addition of CNTs, indicating a rather inert chemical nature of the CNTs in the matrix. However, excessive use of DA caused significant lowering of the T_g, and hence, caution must be taken when using DA for improving CNT dispersion. From sample to sample, the mechanical properties of the CNT composites vary in amounts which are within the limits of the standard deviation. Hence, it can be safely said that the properties of the nanocomposite samples did not improve by addition of CNTs unlike many previous reports. This study, therefore, reveals the difficulty and challenges in the applicability of CNTs in epoxy composites as reinforcing agent. In particular, it is suggested that a good CNT dispersion needs to be stabilised in the epoxy matrix throughout the curing process which has not received sufficient attention till date. Further studies are needed to better understand the mechanisms which cause the destabilisation of CNT dispersions in epoxy resins during curing process.

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